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THERMAL REACTIONS OF THE MIXED-VALENCE IRON FLUORIDES, $Fe_2F_5.NH_3$ --ETC(U)

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by

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20. Abstract

dehydrations lead to the previously reported phases A and B, but the formation of these materials is accompanied by both oxidation and fluoride loss. Vacuum dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ leads to a fully mixed-valence monohydrate phase, A' , which was previously prepared by dehydration in an HF atmosphere. Dehydration of the authentic, crystalline, $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ is seen to be distinguishable from the second stage dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$. Both the thermogravimetric analyses and the kinetic parameters extracted from the several thermal techniques demonstrate that these two forms of " $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ " differ significantly in their thermal reactions.

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Introduction

In 1958 Brauer and Eichner reported² that the reaction of iron powder with hot concentrated hydrofluoric acid led to a yellow crystalline material of composition $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$. This material could be thermally dehydrated to a red trihydrate and, at higher temperatures, to a blue-grey anhydrous material. Since color changes of this sort in a mixed-valence material are suggestive of interactions among the metal ions, we initiated studies^{3,4,5} of the electronic, magnetic, and structural behavior of these systems.

Although the preparation of the yellow heptahydrate was facile using Brauer and Eichner's method², we were unable to reproduce the anhydrous material, and it was apparent that the red material was, at least nominally, a dihydrate rather than a trihydrate. In order to determine the phases which could actually be formed, we have investigated the thermal behavior of these materials in some detail, and find that they are much more complicated than originally reported. While this work was in progress, two reports^{6,7} on the thermal decomposition of the heptahydrate have appeared. Although certain aspects of our work are in agreement with these reports, there are significant differences as well, and one of the purposes of this report is to clarify these differences. We have examined these materials using thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC). These measurements, combined with the physical characterization of products derived from the thermal reactions of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$, have allowed us to both identify these products and determine aspects of the thermodynamics and kinetics of their formation.

Results and Discussion

The initial dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$. Figure 1 shows a typical tracing of the TGA curve observed for $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ under conditions of inert gas flow (N_2 or He) and slow heating rates ($2^\circ\text{C}/\text{min}$). It may be seen that under these conditions two major thermal processes exist. The first of these (ca $80\text{--}130^\circ\text{C}$) corresponds to the loss of approximately five waters of hydration, and suggests formation of the dihydrate $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$. Although Brauer and Eichner reported² that the dehydration proceeded to a trihydrate level, it is clear both from this TGA work and other published reports^{6,7,8} that a dihydrate formulation is more appropriate.

Close examination of Figure 1 demonstrates that this process is clearly not a simple dehydration. In particular, there is a distinct shoulder present at ca 110°C . The position and structure of this shoulder are sensitive to several experimental variables, including the physical properties of the sample and the heating rate employed. Slow heating rates ($\leq 5^\circ\text{C}/\text{min}$) are necessary to attain resolution of this shoulder, and the process is also better-resolved when using samples with lower average crystallite diameter. There is no evidence of this shoulder in the thermograms reported⁷ by Gallagher and Ottaway, but this is probably a result of the conditions used ($10^\circ\text{C}/\text{min}$ heating rate and low sensitivity.) Charpin and Macheteau⁶ employed conditions similar to our own, and the shoulder is clearly present in their published thermogram, although no comment is made concerning its presence. Although the magnitude of this shoulder is variable, it typically represents an approximately 2-3% effect, or roughly one-third to one-half of a mole of water.

The complexity of this first dehydration process is shown more clearly by derivative TGA. Figure 2 represents a DTGA scan of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ at a heating rate of $10^\circ\text{C}/\text{min}$. Of course, at these higher heating rates the entire weight loss curve is shifted to higher temperatures, but even at these high heating rates the shoulder observed by TGA is well resolved, appearing as a distinct process

at ca. 135°C. Furthermore, the curve for the major (low temperature) process is quite asymmetric, suggesting complexity to that process as well. Figure 3 shows the DTGA for that low-temperature process at a heating rate of 2.5°C/min, and it is clear that at least three distinct thermal reactions are occurring between 60 and 100°C. Some complexity is expected, since the transformation from $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ (formulated³ as $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}[\text{FeF}_5\text{H}_2\text{O}_2]^{-}$) to $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ (which contains water bound to Fe^{+2} only⁴) requires loss of water from both Fe^{+2} and Fe^{+3} . These two processes, at least, would be expected to occur at different temperatures and hence lead to some fine structure in the DTGA.

Although the loss in weight between 70 and 150°C is conveniently represented as a transformation of the heptahydrate to the dihydrate, several lines of evidence indicate that hydrogen fluoride evolution is occurring as well as water loss. We have observed HF in the mass spectrum of the evolved gases, and have, at least semi-quantitatively, measured the extent of HF evolution by trapping the TGA effluent gas in a polypropylene trap at -196°C. Acid was determined by titration with NaOH, and fluoride was determined using an ion-specific electrode. The most compelling evidence in favor of a F-deficient iron fluoride product is, of course, accurate elemental analysis of the product. Although the product obtained by heating $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ to the expected dihydrate level (representing a loss of 27.1% of the original sample weight) produces a material having an x-ray powder diffraction pattern identical to that of the authentic dihydrate (i.e., the crystalline dihydrate produced directly⁴ from the high temperature reaction of Fe and HF) the elemental analysis quite clearly demonstrates a substantial deficiency in fluorine ($\text{F}/\text{Fe} = 2.33 \pm 0.05$). There is evidence from other published reports for this fluoride deficiency. Thus, Sakai and Tominaga report⁸ analytical data supporting a ratio $\text{F}/\text{Fe} = 2.41$. Although the ratio reported⁶ by Charpin and Macheteau is not F-deficient

(2.53), the estimated errors are rather large. Gallagher and Ottaway report⁷ no analytical data on the dihydrate. However, their analytical method for fluoride in the heptahydrate required an initial dehydration. They reported that unless the dehydration were performed in an HF atmosphere the method gave inconsistent results, an observation compatible with fluoride loss upon normal dehydration.

It is tempting to equate the shoulder at 110°C in the TGA (Figure 1) with the HF evolution step, since the magnitudes of the effects are comparable. However, we have as yet been unable to distinguish the exact point where fluoride is evolved.

Vacuum Dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$. A thermogravimetric scan of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ obtained under a partial vacuum (ca. 0.1 torr) shows (Figure 4) the onset of dehydration at ca. 60°C, rather than at 80°C. In addition there appears to be rapid loss of weight corresponding to the loss of approximately six moles of water between 60°C and 110°C, but above this temperature interval a smooth and apparently continuous decomposition of the sample appears to occur. No evidence of a shoulder is observed at any point in the thermogravimetric scan, suggesting that the mechanism of solid-state decomposition may be different for samples treated under reduced pressure in the absence of an inert-gas flow. This is consistent with the view that dehydration in vacuo is an equilibrium process, whereas thermal dehydration at atmospheric pressure is an irreversible process involving an activation step.

In an attempt to discover a route to the pure dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$, a sample was placed in an Abderhalden apparatus under vacuum in refluxing ethanol (B.P. = 78°C) for several hours. A product was formed at the approximate monohydrate level, with a purple-grey color. Chemical analysis for both Fe^{+2} and total iron has shown that this material is fully mixed-valence. Continued thermolysis for several days results in a product having a slight fluorine deficiency. Our analyses

support the fluorine-deficient formulation as approximately $\text{Fe}_2\text{F}_{4.8}(\text{OH})_{0.2}\cdot\text{H}_2\text{O}$. Interestingly, X-ray powder diffraction studies show that this "monohydrate" is very similar to a purple-grey phase produced⁷ from an isothermal decomposition of $\text{Fe}_2\text{F}_5\cdot 7\text{H}_2\text{O}$ at 90°C in flowing HF. Although the authors of this study have described the phase (A') as an "anhydrous" product, they have no analytical support for this. It is suggested, on the basis of our studies, that they have produced an authentic, mixed-valence monohydrate, $\text{Fe}_2\text{F}_5\cdot\text{H}_2\text{O}$. In view of the reported dark color of this iron fluoride hydrate, complete characterization of its chemical and physical properties would be interesting. We are presently pursuing further physical studies on this substance and hope to report the results of this investigation at a later date.

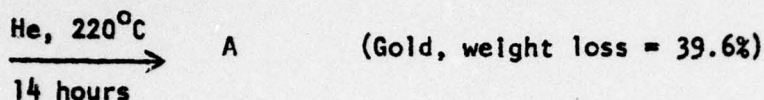
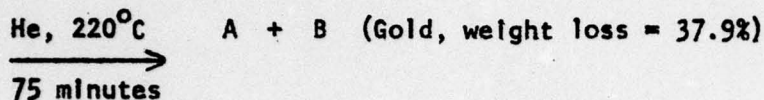
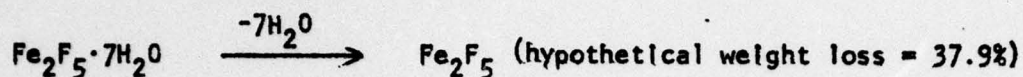
The Second-Stage Dehydration of $\text{Fe}_2\text{F}_5\cdot 7\text{H}_2\text{O}$. Starting at about 180°C , a second major thermal process occurs in the dehydration of $\text{Fe}_2\text{F}_5\cdot 7\text{H}_2\text{O}$ (Fig. 1). A relative plateau is attained at about 220°C after this process is completed, although a slow but continuous weight loss is observed at higher temperatures. A visual examination of the product shows that it has a distinct yellow or light gold color which darkens as the thermolysis is continued until a brown product is produced at elevated temperatures ($> 300^\circ\text{C}$). As can be seen in Fig. 1, the weight loss during this thermal process ($180\text{--}220^\circ\text{C}$) corresponds to the formation of a (nominal) hemihydrate. Repeated measurements of this weight loss lead reproducibly to the formal loss of 6.5 ± 0.1 moles of water. This may be contrasted to the report⁷ by Gallagher and Ottaway that the material at the same point is the fully anhydrous Fe_2F_5 and to the reported⁶ formation of a monohydrate by Charpin and Macheteau⁹. Of course, this overall process requires care in interpretation, since it is not a pure dehydration. As mentioned above, the first stage of the thermolysis involves HF evolution, and the second stage (vide infra) involves both fluoride loss and iron

oxidation.

Gallagher and Ottaway described⁷ the formation of an "off-white" product at 200°C which quickly turned purple-grey as the temperature was increased to 220 and 250°C. X-ray powder diffraction patterns of the products of thermal scans (N₂ flow, 10°C/min) allowed them to identify the products as mixtures of two distinct phases: a relative low-temperature phase (B) which appeared to maximize at about 200°C, and a higher temperature phase (A) which maximized at about 250°C. We have attempted to produce the low-temperature phase (B) through the use of an isothermal dehydration. Reaction conditions of 170°C for 8 hours in a helium flow were chosen, in part because similar conditions were reported⁶ to lead to a monohydrate having the powder pattern of phase B. Although phase B is certainly present in the material we prepare, the material is significantly fluoride deficient. Experimental observations of the bulk weight loss upon heating, elemental analyses, and careful examination of the powder pattern favor formulation of the product as a mixture of phase B and phase A' (the material prepared by vacuum dehydration at 78°C). Continued heating appears to involve a slow oxidation of phase A' to a yellow anhydrous product containing trivalent iron. Although dehydration periods of up to three days have been employed in an attempt to prepare a pure sample of phase B, analyses suggest that approximately 15% of the dehydration product remains in a mixed-valence formulation of low water content. Based on these data, we believe that phase B is a fully-oxidized, fluoride-deficient, anhydrous material. Although we have not been able to prepare the compound in a pure form, our evidence supports the approximate formulation of phase B as Fe₂F₄O.

In agreement with Gallagher and Ottaway⁷, we find that thermolysis at higher temperatures leads to the transformation of phase B to phase A. For example,

Isothermal studies proceed as follows:



Analytical evidence supports the view that the products formed under these conditions are fluorine-deficient materials which undergo slow but continuous decomposition, even beyond the fully "anhydrous" level (i.e., based on Fe_2F_5). We are forced to conclude that the "blue platelets" formulated² as Fe_2F_5 by Brauer and Eichner are not accessible by thermal dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$. It is interesting to note that long isothermal periods at 220°C are accompanied by the appearance in the x-ray powder diffraction patterns of an intense reflection at $d=3.33$ which is totally unique in the iron fluoride systems. The origin of this line is unknown at present.

In summary, our findings concur with the more general belief that the materials $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ exist as well-defined compounds, although the latter must be produced either by the direct preparation described² by Brauer from HF and Fe or by a modification thereof which we have previously described⁴. The thermal dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ is a complex process which occurs in two major stages. Both stages are accompanied by solid-state reactions which result in the liberation of HF when thermolysis is effected under inert atmospheres. It is possible to identify at least three lower hydrates according to X-ray diffraction information: phases A, A', and B, although phase A may not be isolable in pure form since it appears

to exist in a state of continuous decomposition under the conditions required for its synthesis. Phases A' and B have been analytically characterized for the first time.

Dehydration of the Crystalline Dihydrate, $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$.

As reported previously⁴, we have prepared and structurally characterized the authentic dihydrate, $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$. Unlike the species prepared by thermal dehydration of the heptahydrate, this material suffers from no fluoride deficiency. Although these two materials give identical X-ray powder patterns, their analytical formulations and thermal behavior are distinct. Figure 5 shows a TGA (N_2 , $5^\circ/\text{min}$) of the crystalline dihydrate, and it is seen to differ from the second-stage dehydration of the heptahydrate in two ways. First, the dehydration proceeds to, and perhaps somewhat beyond, the fully anhydrous level. Unlike the second-stage dehydration of the heptahydrate, there is no indication of a stable "hemihydrate" stage. Second, the dehydration of the crystalline dihydrate occurs at significantly higher temperatures. The inflection point of the weight loss curve in Figure 5 is ca. 245°C , whereas the comparable point in Figure 1 is ca. 195°C . This difference is due in part to the higher crystallinity of the authentic dihydrate, and, in fact, a thorough grinding of the compound lowers the inflection point by approximately 20°C . Even under these conditions, however, the dehydration occurs at a significantly higher temperature than for the analogous process in the thermolysis of the heptahydrate. The difference in behavior between these two forms of the dihydrate is further manifested by the thermodynamic and kinetic parameters of the dehydration, and will be discussed in more detail below. Not surprisingly, X-ray powder patterns demonstrate that the ultimate products of the thermal decomposition of both of these forms of the dihydrate are the same. (Of course, X-ray powder measurements might not detect small amounts

of another species, or larger amounts of such a species if formed in an amorphous state.)

Thermodynamics of Dehydration. Both stages of the dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ are endothermic processes, as determined by both differential thermal analysis and differential scanning calorimetry. The enthalpy of the low temperature ($<150^\circ\text{C}$) process is measured by DSC to be 66 ± 2 kcal/mole. This number compares favorably with expectations, given typical values¹⁰ of 12-13 kcal/mole for the enthalpy of dissociation of water in crystalline hydrates. For a pure dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ to $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$, then, an enthalpy of ca 62.5 kcal/mole is expected, in rather good agreement with the experimental result. As noted above, this process is not a pure dehydration, but both the small amount of HF liberated, as well as the expected similarity in enthalpies of bonding to the metal center for both H_2O and HF, suggests that the observed value should not differ significantly from expectations based purely on H_2O loss.

DSC data substantiate the difference between the two different forms of the "dihydrate". As noted previously, the second-stage dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ via TGA proceeds to a nominal hemi-hydrate level. Assuming, again, that this process represents a pure dehydration, it corresponds to the loss of 1.5 moles of water, and the expectation of an enthalpy for the process of ca 19 kcal/mole. The experimental value, $\Delta H = 16$ kcal/mole, is in reasonable agreement. More important than the absolute value is the comparison to the authentic, crystalline, dihydrate. This latter material was shown to proceed to the anhydrous level, corresponding to the loss of 2.0 moles of water. The expected enthalpy for the dehydration of the crystalline dihydrate is then ca 25 kcal/mole, close to the experimental value, determined by DSC, of 27 kcal/mole. DSC, like TGA, thus clearly distinguishes

these two materials which have been referred to as the dihydrate, $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$.

Kinetics of Dehydration. Although the kinetic parameters of gaseous or solution reactions are typically examined at a series of constant temperatures, much the same information is available in a single thermogravimetric or thermoanalytical scan. Thus, in principle, a single TGA or DSC experiment provides both activation energy and order of reaction, and certain advantages accrue when all of this information can be attained using a single sample in a single experiment¹¹. In this work we have used four distinct methods to evaluate activation energies, three based on thermogravimetry and one based on differential scanning calorimetry.

Various methods for determining kinetic parameters from non-isothermal TGA measurements have been proposed. The basic assumption, that the rate of a solid state reaction (equation 1) is proportional to some power function of the fraction of



material remaining (equations 2 and 3), is sound, but the means of dealing with the

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (2)$$

$$k = A e^{-E/RT} \quad (3)$$

resulting differential equation differ widely. Some approaches require information only from the TGA curve (so-called integral methods) while others require in addition the derivative of the TGA curve (differential methods). It is also possible to determine kinetic parameters independently using differential scanning calorimetry.

Coats and Redfern¹² have pointed out that there are four reasonable reaction orders for a solid stage process such as described by equation 1. For a zero order process they have derived equation 4. A plot of the left hand side of the equation

$$\log \left[-\log \frac{(1-\alpha)}{T^2} \right] = \log \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (4)$$

versus the reciprocal of the absolute temperature should give a line whose slope is related to the activation energy. From the intercept, the pre-exponential factor can be determined as well. The Coats and Redfern method requires data only from

the TGA curve. For reaction orders n of $1/2, 2/3$ and 1 , equation 5 is used in the

$$\log \left[\frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (5)$$

same way.

A somewhat more general treatment has been given by Freeman and Carroll¹¹ (equation 6). Using both the TGA and DTGA curves, it is possible using equation 6

$$\frac{\Delta[\log(da/dt)]}{\Delta[\log(1-\alpha)]} = n - \frac{E}{2.3RT} \left[\frac{\Delta(1/T)}{\Delta[\log(1-\alpha)]} \right] \quad (6)$$

to determine the activation energy as well as an apparent reaction order. This method has been criticized for being sensitive to experimental conditions. A comparison between the Coats and Redfern and Freeman and Carroll methods is useful in a reaction with reasonable reaction order and activation energy.

A somewhat less general treatment, but one which is useful in its simplicity, has been suggested by Tang.¹³ This method assumes a first order process (equation 7).

$$\log \left[\frac{da/dt}{(1-\alpha)} \right] = \log A - \frac{E}{2.3RT} \quad (7)$$

In the complex process of cellulose and lignin oxidation, Tang's method was used to find inflection points in the activation energy plots which were attributed to

different mechanisms for this solid state reaction. The validity of the Tang treatment, which is of the differential category, can be checked against the integral Coats and Redfern first order method.

Quite independently, DSC provides a second approach to kinetic parameters for solid state reactions. One approach has been described by Rogers and Smith.¹⁴ Their approach allows for either calculating the activation energy and reaction order, or specifying a reaction order. It is also possible using their method to calculate activation energies as a function of temperature in order to observe inhibition or acceleration effects. While there is no overwhelming support for any one of the above mentioned treatments, a comparison of one or more methods is very useful in making meaningful interpretations of solid state reactions.

The activation energies derived using these non-isothermal kinetic methods are presented in Table 1 for three distinct processes. The interpretation of these data requires some care. In the absence of an established mechanism for a solid-state reaction, it is important to obtain an approximate reaction order, since without such information the interpretation and value of calculated kinetic parameters is limited, particularly if the derived reaction order differs significantly from unity.¹⁴ In the case of the first stage dehydration, e.g., $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O} \longrightarrow \text{"Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O"}$, reaction orders calculated using the Freeman-Carroll technique¹¹ are highly variable, falling in a range from ca 0.3 to 5.0 for different samples and experiments. By contrast, reaction orders for both the second stage dehydration and the dehydration of the crystalline dihydrate, which appear to be relatively clean processes, tend to lie in a fairly limited range near 1. The complexity of the first dehydration of the heptahydrate is also reflected in the rather large uncertainties associated with the activation energies. The values in Table 1 represent averages of at least six experiments, and for this process values of specific experiments are highly

dependent on experimental conditions (e.g., heating rate, crystallite size.) Figure 6 shows kinetic data for this process evaluated by the Coates and Redfern method for an experiment involving low heating rates. In this case, the data have been treated assuming a first-order reaction. The presence of two straight-line segments demonstrates resolution of the two major process, and may be compared to the TGA data reported above. Activation energies calculated for the two steps are 21.6 and 79.4 kcal/mole, and indicate clearly that values calculated in the absence of this resolution will have little meaning.

Kinetic parameters evaluated from both the second stage dehydration of the heptahydrate and the dehydration of the crystalline dihydrate show a much better precision, suggesting that their dehydrations are relatively simple processes. Furthermore, activation energies calculated by different methods from thermogravimetric data are in reasonable agreement with activation energies calculated from DSC data, so that we feel confident of these values. There is, however, a large difference between activation energies for the chemical processes, being ca 50 kcal/mole for the second stage dehydration of the heptahydrate, and ca 32 kcal/mole for the dehydration of the crystalline dihydrate. This difference further substantiates the observation, from TGA and enthalpic measurements, that these two processes, although nominally equivalent, are in fact quite distinct.

In summary, this work has shown that the thermal reactions of the mixed-valence iron fluorides are much more complex than previously reported. In particular, the initial dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ has been shown to be a multistep reaction, and to involve some loss of hydrogen fluoride as well as loss of water. The material prepared in this dehydration, nominally $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$, is seen to differ significantly from the authentic dihydrate prepared by an alternative route. Several other phases of lower water content are formed at higher temperatures, their specific distribution depending upon the detailed experimental conditions.

Experimental Section

Materials. $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ ² and $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ ³ were prepared as described previously. Total iron was determined by permanganate titration following stannous chloride reduction or spectrophotometrically with o-phenanthroline following hydroxylamine reduction. Iron (II) was determined spectrophotometrically with o-phenanthroline and iron (III) was determined by difference. Fluoride was determined using an Orion 94-01 fluoride-specific ion electrode.

Thermal Analysis Equipment. The differential scanning calorimetry (DSC), thermogravimetric (TGA) and differential thermogravimetric (DTGA) curves were obtained from a Perkin-Elmer DSC-1b differential scanning calorimeter and TGS-1 thermal balance. Heating rates of 2-10°/minute were employed, using 3-6 mg of powdered sample in an Al_2O_3 crucible in a helium atmosphere. TGA curves were also obtained using a DuPont 900 Thermal Analyzer coupled to a DuPont 950 Thermogravimetric Analyzer. In this case larger samples (ca 20-30 mg) on platinum pans were used, in either helium or nitrogen atmospheres and at heating rates of 2-10°/minute.

TGS-1 Thermobalance - Teflon needle valves replaced the screw cap closures on the gas inlet and tareloop of the TGS-1 in order to provide improved conditions for a pure He atmosphere within the balance bottle. A small platinum heater was used in the modified furnace mount assembly after the suggestions of Etter and Smith¹⁵. Room temperature vulcanizing silicon elastomer was used to seal the furnace screw cap closures.

Microcrucibles (Mettler) were used to replace the platinum sample pans provided by Perkin-Elmer. These crucibles were made of hot pressed Al_2O_3 (approximately 150 mg. in weight). This allowed for small size sample (3-6 mg.). In order to obtain the maximum thermal equilibrium, helium was used as inert gas. Although the rated range of the Cahn RG balance is 20 micrograms full scale (0.1 microgram sensitivity) in

practical terms, the 0.4 mg. range (0.4 microgram sensitivity) represents a maximum sensitivity of this system. Either a Texas Instrument 2 Channel Recorder (Servo Riter II, 1 millivolt range) or a multiplexed 4 Channel Heath Recorder was used to record the output from the Cahn RG balance.

The derivative of the primary (unattenuated) TGA signal was fed into a Cahn Mark II Time Derivative Computer (classical RC differentiation) and the output of this device was recorded on the second channel of the TI Recorder or a second multiplex channel on the Heath Recorder (1 or 10 mv respectively). The approximate ranges on the Time Derivative computer were calibrated by determining weight loss due to diffusion of water vapor from a Kneudsen cell at a controlled temperature. The balance weight ranges were calibrated Class M (NBS) standard 10 mg. weights.

Temperature calibrations of the thermal balance were obtained by means of the Curie point magnetic transitions. Over the temperature range of 100°-500° the observed and actual temperature, agreed to within $\pm 1^\circ$ (He atmosphere, 10°/min or less heating rate).

Sample Loading Procedure - The sample crucible was first heated to a temperature of approximately 800° in air, then allowed to cool to room temperature, and suspended from the balance. The mass dial of RG balance was adjusted so that zero deflection was noted on a recorder scale when the atmosphere of helium had been reestablished in the balance chamber. The sample was then loaded on the balance, being protected from the atmosphere by increasing the flow of helium. When the sample was in place and the hangdown tube was returned to its normal position, the helium flow was maintained at 20 ml. per minute for approximately 5 minutes, at which time the balance chamber again contained a pure helium atmosphere. Then the sample weight could be obtained directly from the recorder. Activation energies obtained by the methods

described above are in agreement with published data on the dehydration of $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, even though smaller samples were used in this study (10 mg. vs. 100 mg.).

X-Ray Powder diffraction. X-ray powder diffraction patterns were obtained with the Straumanis technique using vanadium-filtered Cr radiation ($\lambda_{\text{mean}} = 2.2909 \text{ \AA}$).

Acknowledgement. Work performed at the University of Vermont was supported by the Office of Naval Research.

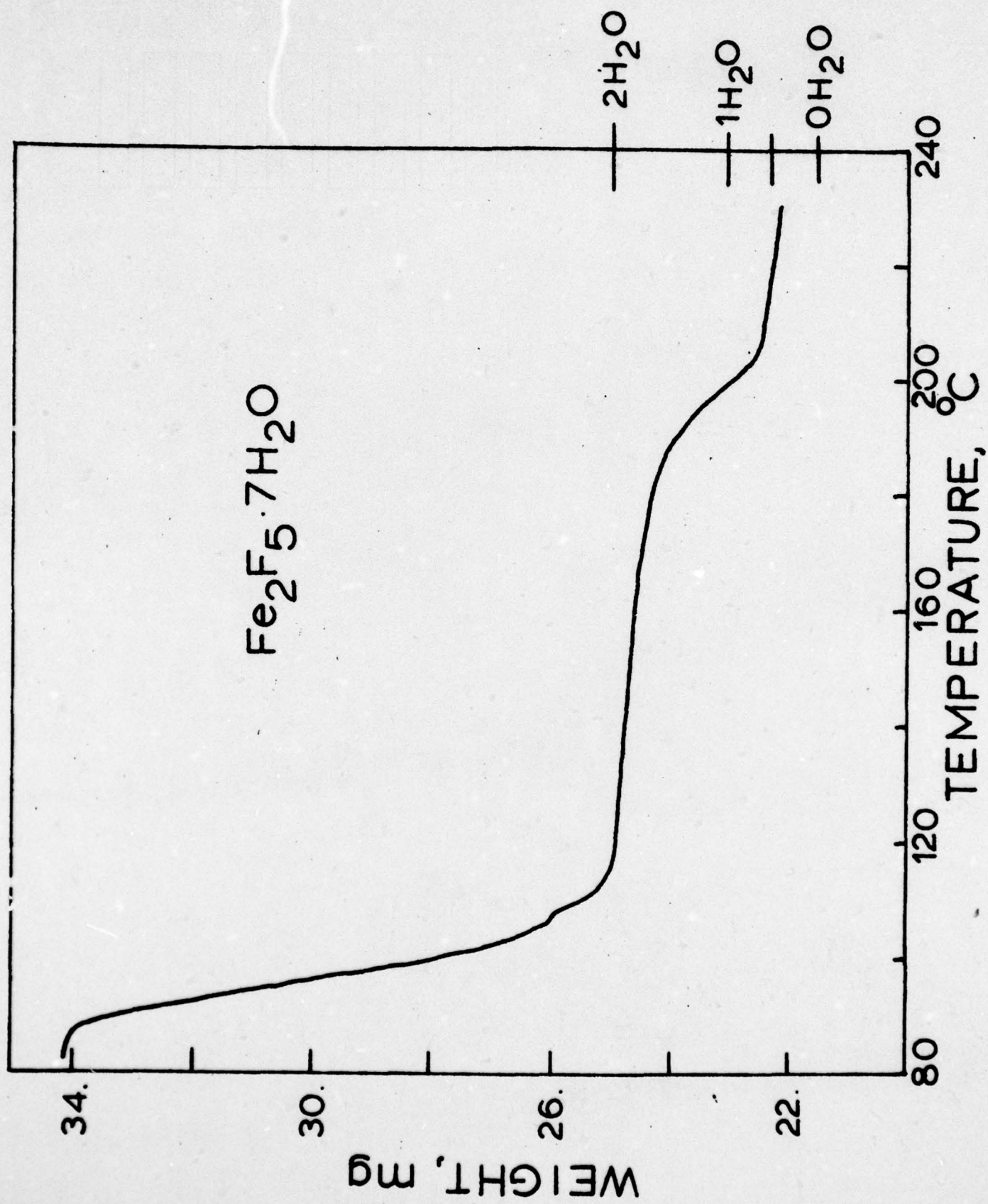
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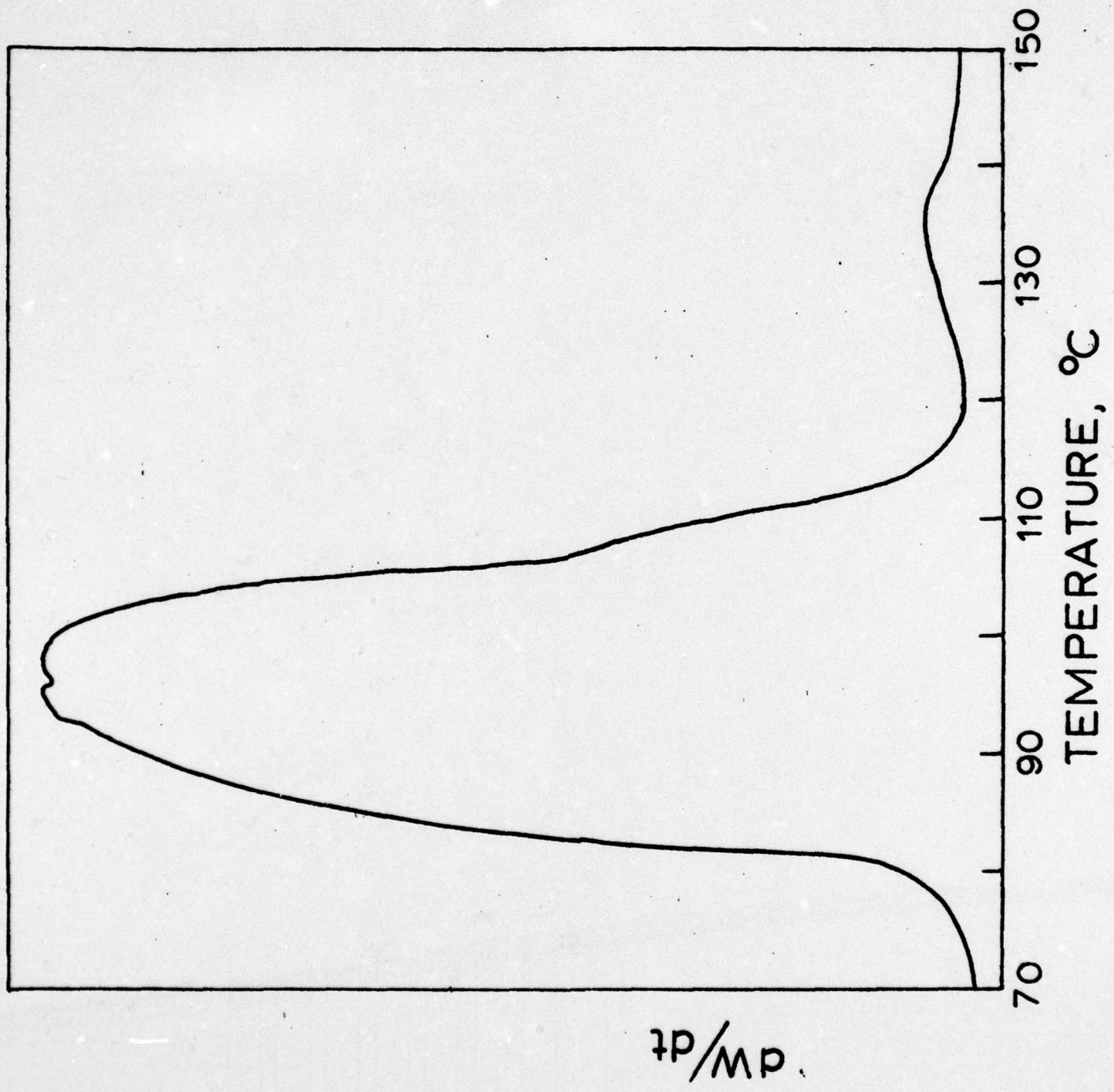
Table 1 - Activation enthalpies for dehydration steps. " $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ " represents the product formed upon the low temperature dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$, and is to be distinguished from the authentic crystalline dihydrate prepared directly from the Fe and HF.

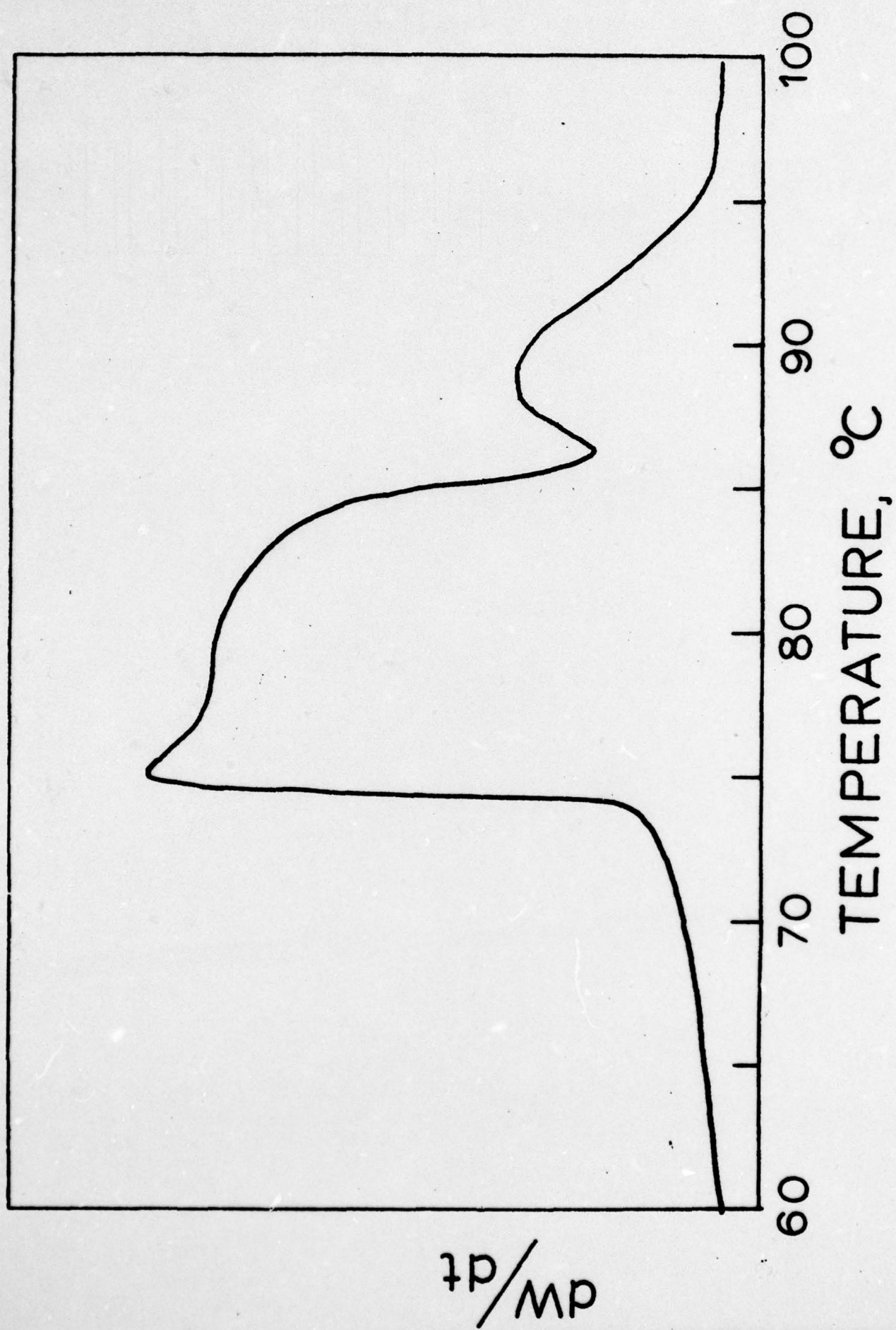
<u>Calculation method</u>	<u>ΔH^\ddagger, kcal/mole (Standard deviation)</u>		
	$\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O} \rightarrow$ <u>"$\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$"</u>	" $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ " \rightarrow <u>"Fe_2F_5"</u>	$\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O} \rightarrow$ <u>Fe_2F_5</u>
Freeman-Carroll	29 (11)	54 (4.5)	31 (2.9)
Tang	42 (11)	47 (2.9)	27.6 (1.4)
DSC	27 (see text)	54	36

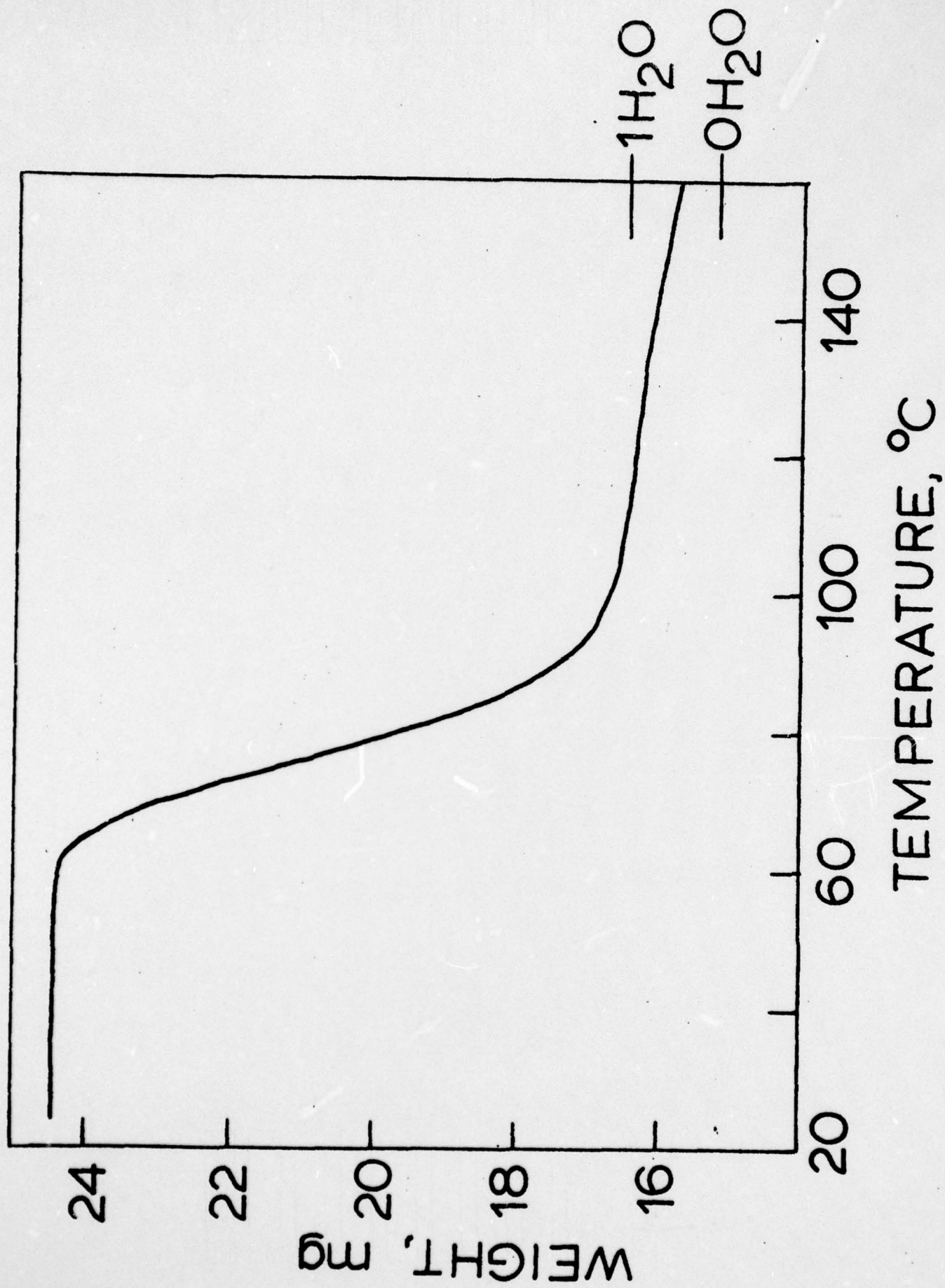
Figure Captions

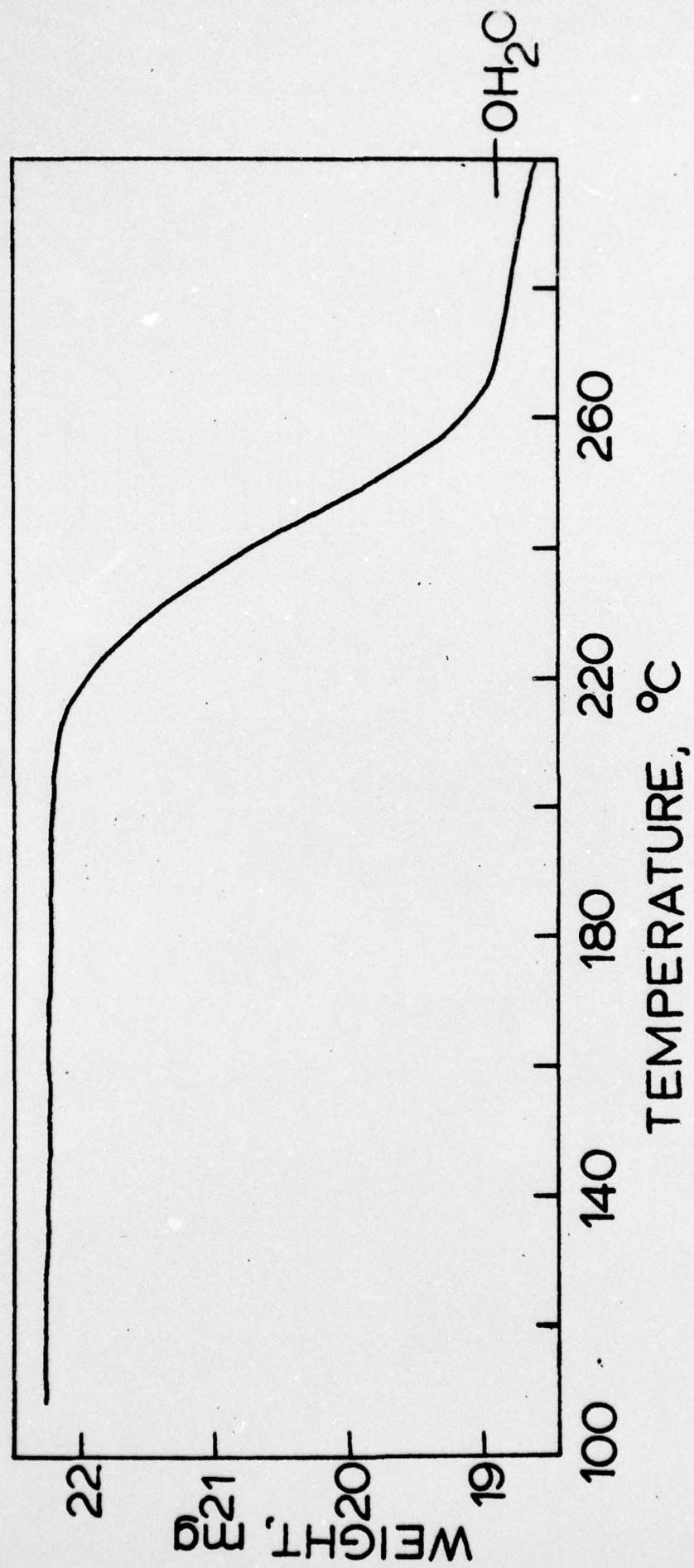
- Figure 1. Thermogravimetric analysis of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ in a helium atmosphere at a scan rate of $2^\circ\text{C}/\text{minute}$.
- Figure 2. Differential thermogravimetric analysis of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ (initial dehydration only) in a helium atmosphere at a fast scan rate ($10^\circ\text{C}/\text{minute}$.)
- Figure 3. Differential thermogravimetric analysis of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ (initial process only) in a helium atmosphere at a slow scan rate ($2.5^\circ\text{C}/\text{minute}$.)
- Figure 4. Thermogravimetric analysis of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ in vacuum, scan rate $1^\circ\text{C}/\text{minute}$.
- Figure 5. Thermogravimetric analysis of the crystalline dihydrate, $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$, in a nitrogen atmosphere, scan rate $5^\circ\text{C}/\text{minute}$.
- Figure 6. First order kinetics for the initial dehydration of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ using the Coats and Redfern method.

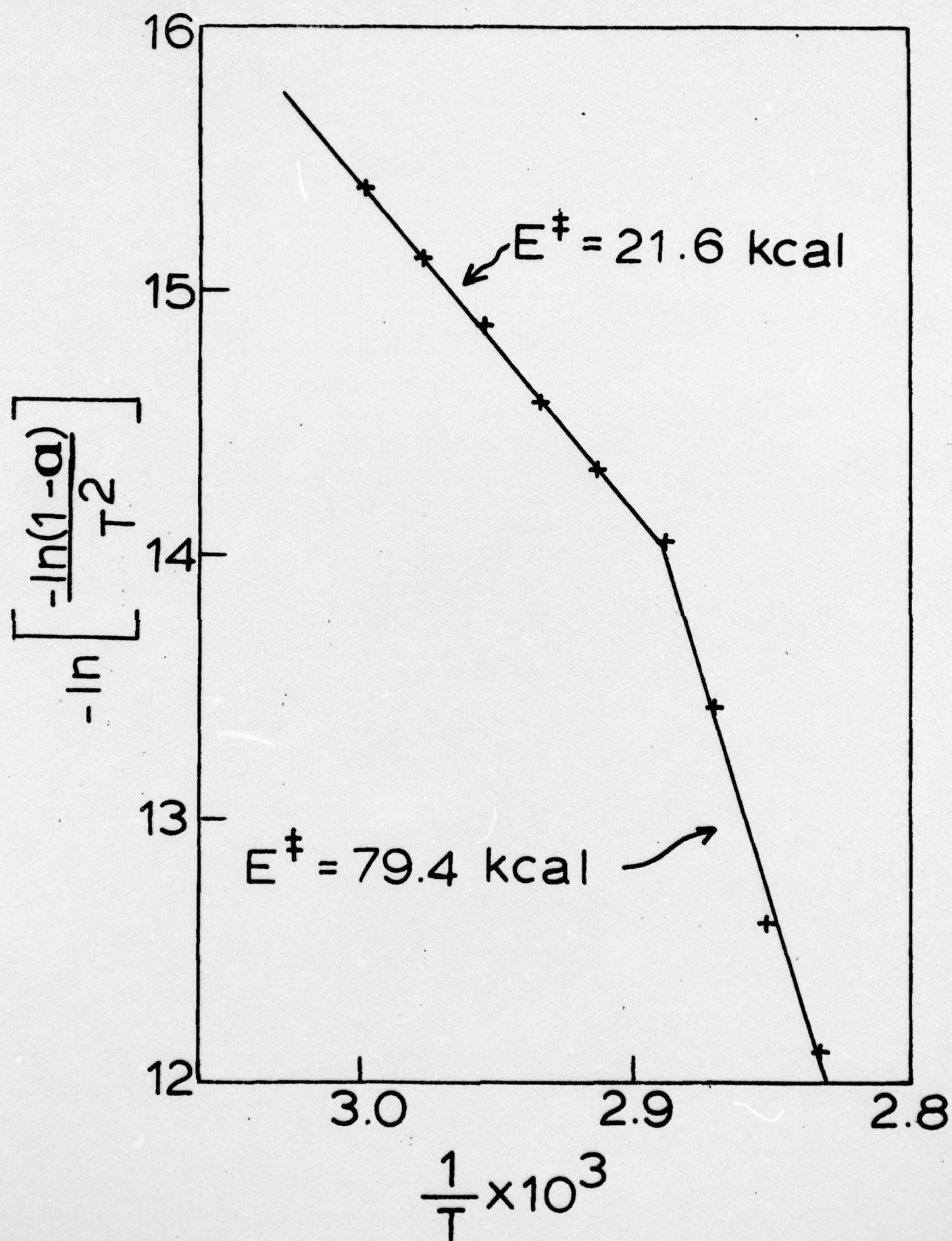












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